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Pesticide Residues on Plants: Correlation of Representative Data as a Basis for Estimation of Their Magnitude in the Environment

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Summary

Data or reliable estimates on the amount of pesticide residues on differing plant species are frequently required in order to evaluate the toxicological significance of a pesticide in the terrestrial environment. This paper includes and correlates data on residues of more than 20 pesticides on more than 60 crops as taken from the literature and from United States crop tolerances. By consideration of differences in vegetative yield, surface to mass ratio, and plant interception factors, crops have been classified into seven differing categories.

Based on the experimental and tolerance data, numerical *Upper Limit* and *Typical Limit* residue values have been assigned for each of these crop categories, both immediately after application and for the interval six weeks after application of pesticide. The *Upper Limit* and the *Typical Limit* residue values on these crop categories are in the following descending order:

range grass ⟩ grass ⟩ leaves and leafy crops ⟩ forage crops ⟩ pods containing ⟨—⟩ seeds ⟩ grain ⟩ fruit

For a pesticide dosage of 1 lb/acre, *Upper Limit* values range from 240 ppm on range grass to 7 ppm on fruit (immediately after application). *Typical Limit* values range from 125 ppm to 1.5 ppm.

The decline of pesticide residues with time has been reviewed within the context of estimating residues at varying periods of time after application of the pesticide. The numerical *Limit* values and consideration of factors affecting decline provide a basis for adequate estimation of the level of residue for other types of plants for which data are unavailable. Estimates based on the above concepts provide for *increased reliability* in defining the toxicological significance of pesticides as related to the food supply of man, domestic animals, birds, and other wildlife. Similarly, the impact of a proposed pesticidal-cultural practice may be evaluated more completely prior to commercialization.

Introduction

The importance of knowing the *quantitative level of residues of pesticides on various plants* has increased dramatically during the past twenty years. Classic interest, both initially and on a continuing basis, has been centered on evaluation of the toxicological significance of possible pesticide residues in the food supply of man. Currently, emphasis also is being placed on evaluating the toxicological significance of pesticide residues in the food supply of domestic animals, birds, other terrestrial wildlife, and fish. Therefore, residues of pesticides today must be viewed within the context of their relation to the total environment.

It follows that either data or reliable estimates pertaining to the level of many different pesticides on a wide variety of plants are needed by ecologists, toxicologists, originators of pest control programs, and the many government and industrial personnel concerned with regulation of the use of pesticides. Many excellent articles contain quantitative data on the levels of residue of specific pesticides on an agricultural commodity or on a relatively small group of agricultural commodities. Similarly, the many conditions affecting pesticide residues, such as the amount and type of formulation applied, timing of application, the physical and chemical properties of the pesticide, and climate, have been studied quantitatively for specific cultural-pesticidal practices. However, the available quantitative data are limited in scope relative to the total environment. Moreover, the literature data lack sufficient correlation to permit ready translation to the many situations for which no residue data are available, such as application of pesticides to non-cultured, naturally growing vegetation or application of a new pesticide prior to obtaining field data.

Thus, the purpose of this paper is to summarize representative available data on pesticide residues and thereby to provide bases for *estimating residues of pesticides on terrestrial plants*. The authors consider that the accuracy of estimations should be sufficient to permit meaningful assessments of the environmental impact of a *pest control program based on research data*, prior to obtaining field development information. Such estimates of pesticide residue levels on diverse food and feed items are a necessary input to *toxicological safety calculations* and evaluations. For examples, see Kenaga (1971).

Literature and Tolerance Data as a Source of Pesticide Residue Information

Sophisticated analytical methodology has been developed during the past two decades for accurately determining trace amounts of almost every pesticide manufactured. In addition, literally hundreds of thousands of individual samples of crops and food commodities have been analyzed to determine the level of residues of specific pesticides. These data delineate residues on individual commodities immediately after application of pesticides, at varying intervals between treatment and harvest, in commercial channels of trade, and occasionally after processing and cooking. Thus, there is an extensive data base upon which to develop correlations of residue levels.

This data base has been considered in two ways in preparing this paper. First, the published literature has been randomly reviewed, but with emphasis on recording levels of residues which were the highest reported for a representative cross-section of experimental and commercial pesticidal-cultural practices. This paper includes illustrative data from 22 articles, although several hundred articles were reviewed. The highest levels of pesticide residues were emphasized in order to represent the most rigorous situations requiring toxicological evaluation of pesticide residues.

The second source of residue information used in preparing this paper was the *list of tolerances and use conditions* published by the United States Department of Agriculture (1968, 1969). Before a pesticide is used commercially on a food crop in the United States, a tolerance value for residues of the pesticide must be established by the United States Food and Drug Administration. The tolerance value is based upon the results of carefully conducted, replicated experiments, usually at several geographical locations. In sampling an agricultural crop, the presence of residue which exceeds the tolerance value would be basis for legal action. For this reason, the tolerance value customarily represents the highest level of residue of pesticide found in many samples from several experiments at a defined time interval after application, rather than the average level of residue. Since analytical methodology is often validated by a second party, and since experiments from several geographical locations represent a variety of climatic variables, the tolerance values often provide a more substantive basis for correlating residue data than some of the literature data citing results of single experiments. Although the *relative toxicity* of a pesticide is a factor in determining whether a tolerance will be established or whether a *harvest time restriction* is needed, it should be emphasized that the actual numerical value of the tolerance is based primarily upon the results of the residue experiments (FDA, 1968).

Bases for Correlating Residue Data

Correlation of the literature data is facilitated by unitizing an important parameter affecting pesticide residue levels, namely, the *amount of pesticide applied (dosage)* to a unit area of cropland (lb/A). On an arithmetical basis, application of a pesticide to a given plant surface area results in residues in direct proportion to the dosage, if other variables are similar and if spray volume is maintained below the point of significant run-off.

This proportional relationship permits translation of residue data to a common basis which we will designate as Residue from a *Unit Dosage*, abbreviated to RUD*. *RUD designates the residue in a food or feed commodity after treatment with a pesticide, the residue being calculated on the basis of a dosage of 1 lb/A.*

$$\text{RUD} = \frac{\text{actual residue}}{\text{treatment rate}} = \frac{\text{ppm}}{\text{lb pesticide/A}}$$

Arithmetically, RUD may be derived from residue data on a crop treated at any practical dosage. For example, if treatment of an apple orchard at the rate of 15 lb malathion/A leads to 12 ppm residue in or on apples, then the RUD is 0.8 ppm.

RUD values provide a convenient basis of comparing residues from different experiments or field situations. It should be noted, however, that the proportional relationship of residue level to dosage is strictly true only when all experimental or field variables other than dosage are similar. Therefore, differences in RUD values indicate variation in one or more of the parameters affecting residue levels.

Consideration of literature data on pesticides indicates that *residue levels* of any pesticide on similar plants are usually of the same order of magnitude if measured immediately after application of the pesticide and if the treatment rates are similar. For example, the Food and Drug Administration has defined more than 25 crop groupings, such as cherries, plums, and prunes; corn and sorghum forage; and citrus fruits (U. S. Code 1967). Crops within a grouping are regarded as somewhat similar and residue data from one crop is often translated as representative of the data expected on other crops in the grouping. These *crop groupings* appear to be based primarily upon taxonomically similar species and are therefore somewhat narrow in scope.

However, the principle of similar residue levels occurring on similar types of plants is useful in correlating residue data and can be extended by considering physical factors relating to plant structure.

Three important *physical factors* significantly affect the level of residue immediately after application of a pesticide to a crop or to vegetative cover. These are the weight of the vegetative cover, the surface area/mass ratio of the food or feed commodity, and the degree of *interception of the pesticide* by soil or by plants or plant portions other than the given commodity.

Each of these factors has been considered

* Getzendaner et al. (1969) and Getzendaner et al. (1968) have used the proportional relationship of residue level to dosage in interpreting residue levels of picloram on grass and of bromide ion in food commodities. They have used the term specific residue to designate ppm picloram/(lb picloram/A) or ppm bromide/(lb CH_3Br/10^3 ft^3 space treated).

individually in the literature by various investigators. For example, Palmer and Radeleff (1969) considered the yield per acre of vegetative cover in translating pesticide dosage to residue level in forage. Kenaga (1968) considered the surface/mass ratio of individual food items as a significant factor affecting residue levels. Morton et al. (1967) in studying spray applications of several herbicides found that two varieties of range grass intercepted only 41 % of the applied dosage. Further, simple comparison of residue levels of 1 to a few ppm pesticide on grains and fruit with the amount of pesticide applied to the crop indicate that protective chaff, husk, or leaves intercept a significant portion of the applied pesticide.

grains fruits

Food and feed commodities, therefore, have been classified into different categories, which represent qualitative differences in vegetative yield, surface/mass ratio, and interception factors. For example, the categories of grass, fruit, and grain are obviously quite different in one or more of these respects. Consideration of such crop categories along with translation of residue data to the basis of a dosage of 1 lb pesticide/A (RUD) provide the bases for correlating the numerical values of pesticide residues reported in this paper.

Residue Values at Unit Dosage (RUD) Derived from Literature and Tolerance Data

Data on levels of residue for 21 pesticides in or on 36 crops from 22 literature sources

Table 1. Residues of Pesticides on Range Grass

Crop	*Pesticide*[1]	*Days Between Treatment & Sampling*	*Application Rate, Lb Pesticide*[2]	*Highest Residue, ppm* Reported	*Highest Residue, ppm* RUD[3]	*Reference*
Range Grass	Dicamba, Amine Salt	0 28	2 2	100 12	50 6	(Morton, et al., 1967)
Range Grass	2,4-D	0 28	2 2	250 50	125 25	(Morton, et al., 1967)
Range Grass (dead undercover)	2,4-D	0 28	2 2	80 8	40 4	(Morton, et al., 1967)
Fodder Grass (West Germany)	Endosulfan	0 0	0.2 0.6	2 55	10 92	(Maier-Bode, 1968)
Range Grass (Montana)	Picloram, Amine Salts	0 14	3 3	720 125	240 42	(Getzendaner, et al., 1969)
Range Grass (7 states)	Picloram, Amine Salts	0 14 56	0.5 to 3 0.5 to 3 0.5 to 3	— — —	135[4] 32[4] 24[4]	(Getzendaner, et al., 1969)

[1] Reference to specific pesticides in this paper is usually by the common, nonproprietary name. Chemical names for insecticides are listed by Kenaga and Allison (1969), for herbicides by The Weed Society of America (1967).

[2] Dicamba, 2,4-D and Picloram are expressed as lb acid equivalent/A.

[3] Residue from Unit Dosage is calculated from $\frac{\text{ppm residue}}{\text{lb pesticide/A}}$.

[4] Average residue values from experiments with 3 different formulations in 7 states.

Table 2. Residues of Pesticides on Leaves and Leafy Crops

Crop	Pesticide	Days Between Treatment & Sampling	Application Rate, Lb Pesticide/A	Highest Residue, ppm Reported	RUD[1]	Reference
Apple Leaves	Parathion	0.04	2.5	250	100	(Fahey, et al., 1952)
	Methyl Parathion	0.04	1.9	138	73	
	EPN	0.04	2.1	263	125	
Tomato Leaves	Parathion	0.	0.9	21.5	24	(Smith, et al., 1952)
	Sulfotepp	0.04	0.45	2.4	5	
Bean Leaves	Endosulfan	0	1.0	88	88	(Maier-Bode, 1968)
Pear Leaves	Endosulfan	0	0.25	0.8	3	(Maier-Bode, 1968)
Spinach	Endosulfan	0	1	21	21	(Maier-Bode, 1968)
Chard	Endosulfan	0	1	57	57	(Maier-Bode, 1968)
Collard	Endosulfan	0	0.75	39	52	(Maier-Bode, 1968)
Cauliflower Leaves	Endosulfan	0	0.75	8.3	11	(Maier-Bode, 1968)
Cauliflower Head	Endosulfan	0	0.75	<0.05		(Maier-Bode, 1968)
Water Cress	Endosulfan	0	0.5	16	32	(Maier-Bode, 1968)
Celery	Endosulfan	0	0.5	1.8	3.6	(Maier-Bode, 1968)
		0	1.0	3.0	3.0	
Celery Leaves	Parathion	0.17	0.13	6.2	50	(Van Middelem and Wilson, 1955)
		0.17	0.13	1.3	8	
Celery Stalk	Parathion	0.17	0.13	0.64	5	(Van Middelem and Wilson, 1955)
Cabbage	Malathion	0.17	0.63	15	23	(Waites and Van Middelem, 1955)
		0.17	1.9	91	48	
		7.0	1.9	24.8	13	
	Parathion	0.17	0.28	10	36	
		7.0	0.28	22.6	9	
Carrot Tops	Endosulfan	0	1	14	14	(Maier-Bode, 1968)
Turnip Greens	Parathion	0.17	0.11	7.1	63	(Waites and Van Middelem, 1955)
		0.17	0.3	31	103	
		7.0	0.3	2.6	9	
Lettuce	Phosdrin	0.17	0.9	12	13	(Coffin and McKinley, 1964)
		1.0	0.9	2	2	
	Diazinon	0.17	0.9	8	9	
		1.0	0.9	6	7	
	Demeton	0.17	0.9	5[2]	6	
		1.0	0.9	2.5[2]	3	
	Trithion	0.17	0.9	8.3[2]	9	(Coffin, 1964)
		1.0	0.9	7.5[2]	8	

Crop	Pesticide	Days Between Treatment & Sampling	Application Rate, Lb Pesticide/A	Highest ppm Reported	Residue, RUD [1]	Reference
	Endosulfan	0	1	59	59	(Maier-Bode, 1968)
		0	3	133	44	
		0	1	11	11	
Lettuce (Immature)	Parathion	0.04	0.9	98	109	(Smith, et al., 1952)
Lettuce (Mature)	Parathion	0.04	0.9	56	62	(Smith, et al., 1952)

[1] Residue From Unit Dosage is calculated from $\frac{\text{ppm residue}}{\text{lb pesticide/A}}$.

[2] Residue includes 3 isomers and metabolite.

[3] Residue includes trithion and 5 metabolites.

Table 3. Residues of Pesticides on Forage Crops

Crop	Pesticide	Days Between Treatment & Sampling	Application Rate, Lb Pesticide/A	Highest Residue, ppm Reported	RUD [1]	Reference
Alfalfa	Endosulfan	0	0.25	14.5	58	(Maier-Bode, 1968)
	DDT	0	1	33 [2]	33	(Ebeling, 1963)
		0	2	65 [2]	33	
		0	4	160 [2]	40	
		0	10	350 [2]	35	
	Dieldrin	0	0.06	2 [2]	33	(Mitchell and Lykken, 1963)
		1	0.06	0.7	12	
	Endrin	0	0.12	3 [2]	25	(Mitchell and Lykken, 1963)
		2	0.12	1.5	12	
		0	0.25	7 [2]	28	
		2	0.25	3.5	14	
	Aldrin	0	0.15	6	40	(Mitchell and Lykken, 1963)
		2	0.15	2.2	15	
		0	0.3	10	33	
		2	0.3	4	13	
Alfalfa (14–20 inches)	Aldrin	0	0.12	2	16	(Dahm, 1952)
		18	0.12	<0.1	—	
	Chlordane	0	1	12	12	(Dahm, 1952)
		18	1	3	3	
	Toxaphene	0	1.5	30	20	(Dahm, 1952)
		18	1.5	14	10	
Red Clover	Endosulfan	0	0.25	8.2	33	(Maier-Bode, 1968)
Birdsfoot Trefoil	Endosulfan	0	0.25	6.8	28	(Maier-Bode, 1968)
Red Clover	DDT	0	2	45	22	(Decker, 1957)

[1] Residue from Unit Dosage is calculated from $\frac{\text{ppm residue}}{\text{lb pesticide/A}}$.

[2] Residues estimated by extrapolation to zero time.

Table 4. Residues of Pesticides on Pods Containing Seeds (Beans)

Crop	Pesticide	Days Between Treatment & Sampling	Application Rate, Lb Pesticide/A	Highest Residue, ppm Reported	Highest Residue, ppm RUD[1]	Reference
Snap Beans	Dimethoate	1	0.25	1.7	7	(de Pietri-Tonelli, et al., 1965)
		3	0.25	1.1	4	
		1	1.0	7.9	8	
		3	1.0	6.8	7	
Green Beans	Endosulfan	0	0.5	2.3	4.6	(Maier-Bode, 1968)
		0	1.0	2.9	2.9	
French Beans	Endosulfan	0	1	1.4	1.4	(Maier-Bode, 1968)
Red Kidney Beans	Endosulfan	0	0.25	1.2	5	(Maier-Bode, 1968)
Green Beans	Endosulfan	0	1.5	1.24	0.8	(Maier-Bode 1968)
Snap Beans	Malathion	0.04	1.75	8.6	5	(Smith, et al., 1955)
		0.6	1.75	1.9	1.1	
Snap Beans	DDT	1	0.6	1	1.7	(Waites and Van Middelem, 1958)
		7	0.6	0.3	0.5	
Green Beans	Methoxychlor	0.04	1.75	21	12	(Wallis and Carter, 1959)
		3	7.8	7.8	4.5	

[1] Residue from Unit Dosage is calculated from $\frac{\text{ppm residue}}{\text{lb pesticide/A}}$

Table 5. Residues of Pesticides on Fruits

Crop	Pesticide	Days Between Treatment & Sampling	Application Rate, Lb Pesticide/A	Highest Residue, ppm Reported	Highest Residue, ppm RUD[1]	Reference
Apricots	Captan	3[2]	7	16.8	2.4	(Kilgou, et al., 1967)
		6[3]	7	2.8	0.4	
Cherries	Dimethoate	0.17	1.8	5.6	3	(de Pietri-Tonelli, et al., 1965)
		1	1.8	6.6	4	
	Endosulfan	0	2.25	15	6 6	(Maier-Bode, 1968)
		0	1.0	4.6	4.6	
Peaches	Dimethoate	0.04	1.1	6.6	6	(de Pietri-Tonelli, et al., 1965)
		1	1.1	6.0	5.5	
	Parathion	0	0.54	0.5	1[4]	(Braid and Dustan, 1955)
		7	0.54	0.25	0.5	
		0	1.1	1.3	1.2[4]	
		7	1.1	0.65	0.6	
		0	1.35	4.3	3	

Crop	Pesticide	Days Between Treatment & Sampling	Application Rate, Lb Pesticide/A	Highest Residue, ppm Reported	RUD[1]	Reference
	EPN	0	1.13	8.3	7	(Fahey, et al., 1952)
Olives	Dimethoate	0	2.6	11.9	4.5	(de Pietri-Tonelli, et al., 1965)
		4	2.6	6.9	2.5	
Apples	Dimethoate	0	5.5	2	0.4	(de Pietri-Tonelli, et al., 1965)
		3	5.5	1.1	0.2	
		0	16.5	5.8	0.4	
		3	16.5	3.7	0.2	
	Endosulfan	0	3.0	2.7	0.9	(Maier-Bode, 1968)
		0	2.2	1.7	0.8	
Grapes	Endosulfan	0	0.5	1.2	2.4	(Maier-Bode, 1968)
Strawberries	Endosulfan	0	4	9	2.3	(Maier-Bode, 1968)
	Methoxychlor	1	1.75	5.5	3.1	(Wallis and Carter, 1959)
Orange (Valencia)	Diazinon	0	8.5	0.9	0.0	(Gunther, et al., 1958A)
Orange (Navel)	Ovex	0	7.5	2.5	0.3	(Gunther and Jeppson, 1954)
	Dioxathion	0.17	4.7	0.7	0.2	(Gunther, et al., 1958B)
		0.17	17.8	1.8	0.1	
Lemons	Diazinon	0	5.6	6.6	1	(Gunther, et al., 1958A)
		1	5.6	3.6	0.6	
	Dioxathion	0	5.6	10.4	1.9	(Gunther, et al., 1958B)
		0	11.2	16.1	1.5	
		0	3.75	1.9	0.5	

[1] Residue from Unit Dosage is calculated from $\frac{\text{ppm residue}}{\text{lb pesticide/A}}$.
[2] Time after the last of 3 applications. Each application at the rate of 7 lb/A. Application rate estimated on the basis of 350 gal. of spray/A.
[3] Time after the last of 2 applications.
[4] Immature fruit.

have been assembled in Tables 1 to 5. Sixty-six *pesticide-crop combinations* are cited. The data represent a selection of values from the literature with emphasis on the highest level of residue reported for a representative cross-section of pesticidal-cultural practices. Pesticide formulations applied as sprays usually give higher residue levels than dust or granular formulations. Therefore, only spray formulations have been considered. Data were also selected to illustrate several of the *variables affecting levels of residue* both immediately after treatment of the crop and at intervals after treatment.

Tables 1 to 5 represent five categories of crops, namely, range grass, leaves, and leafy crops, forage crops, pods containing seeds (beans), and fruit. These five categories, although somewhat empirical, have been based upon the concepts noted earlier that residues in plants are related to vegetative interception factors, to the ratio of surface/mass, and to the vegetative yield per acre. Within each crop category of Tables 1 to 5 all of the RUD values for samples harvested on the day of pesticide treatment have been compared. The highest value of RUD and the mean value for each cate-

gory are shown in Table 6. The data indicate that the level of residue decreases in the following sequence:
range grass > fruit and vegetable leaves > forage crops (alfalfa, clover) > pods containing seeds (beans) > fruit.

The residue data in Tables 1 to 5 represent different pesticides and different crops. Although the mean value correlations in Table 6 have no theoretical relationship to the way in which the unrelated experiments were conducted, we believe the fact that the similarity in the relationship of the sequence of mean values to the highest RUD values supports the empirical classification of the crop residue data.

As a further test of the correlation of residue levels with crop classification, the *United State tolerance* (USDA 1968, 1969)

Table 6. Correlation of Representative Literature Data: Highest and Mean Values of RUD According to Crop Category (samples collected the day of pesticide treatment)

Crop Category	*RUD, Highest Residue*	*ppm lb Pesticide/A Mean Residue Value*
Range Grass	240	92 to 125
Fruit and Vegetable Leaves	125	32
Forage Crops (Alfalfa, Clover)	58	33
Pods Containing Seeds (Beans)	12	4
Fruit	6.6	1.5

Table 7. Residues of Pesticides on Small Fruit as Derived from Crop Tolerance Values and Recommended Treatment Rates (USDA, 1968, 1969)

Pesticide	*Crop*	*Highest Application Rate, Lb Pesticide/A*	*Tolerance Value, ppm*	*Restriction-Days Between Treatment and Harvest*	*RUD [1], ppm*
Carbaryl	Cherries	6	10	1	1.7
	Cranberries	4 (dust)	10	1	2.5
	Dewberries	2	12	7	6
	Grapes	3	10	0	3.3
	Loganberries	2	12	7	6
	Plums	6	10	1	1.7
	Raspberries	2	12	7	6
	Strawberries	2	10	1	5
Kelthane	Blackberries & Boysenberries	1.2	5	2	4
	Dewberries	1.2	5	2	4
	Grapes	1.2	5	7	4.1
	Loganberries	1.2	5	2	4.1
	Plums	2	5	7	2.5
	Raspberries	1.2	5	2	4.1
	Strawberries	2.4	5	2	2
Toxaphene	Blackberries & Boysenberries	4	7	45 [2]	1.75
	Cranberries	5	7	45 [2]	1.4
	Loganberries	4	7	45 [2]	1.75
	Strawberries	2	7	1	3.5
		5	7	3	1.4

Pesticide	Crop	Highest Application Rate, Lb Pesticide/A	Tolerance Value, ppm	Restriction-Days Between Treatment and Harvest	RUD[1], ppm
DDT	Blackberries	2	1	45[2]	0.5
	Blueberries	2	7	21	3.5
	Boysenberries	2	1	45[2]	0.5
	Cherries	12	3.5	30	0.3
		16	3.5	42	0.2
	Grapes	5	7	40	1.4
	Plums	12	3.5	30	0.3
	Strawberries	4	1	45[2]	0.25
Malathion	Blackberries & Boysenberries	4	8	1	2
	Blueberries	2.5	8	1	3.2
	Cherries	8	8	3	1
	Cranberries	2.5	8	3	3.2
	Currants	2.0	8	1	4
	Dewberries & Loganberries	4	8	1	2
	Gooseberries	2	8	3	4
	Grapes	2.75	8	3	2.9
	Plums	10	8	3	0.8
	Raspberries	4.5	8	1	1.8
	Strawberries	2	8	3	4
Parathion	Blackberries, Boysenberries, Dewberries	1	1	15	1
	Blueberries	0.6	1	14	1.7
	Cherries	2.1	1	14	0.5
	Cranberries	0.8	1	15	1.3
		1.0	1	30	1
	Currants	0.8	1	30	1.3
	Grapes	1.5	1	14	0.7
		2.5	1	45[1]	0.4
	Plums	4	1	14	0.25
	Raspberries	1	1	15	1
	Strawberries	0.8	1	14	1.3
Methyl Parathion	Cherries	2.5	1	14	0.4
	Gooseberries	1	1	15	1
	Grapes	0.75	1	14	1.3
	Plums	4	1	14	0.25
	Strawberries	0.75	1	14	1.3
Demeton	Grapes	0.38	1.25	21	3.3
	Plums	2 (x 3 times)	0.75	30	0.38
	Strawberries	0.38	0.75	21	2

[1] Residue from Unit Dosage is calculated from $\frac{\text{ppm residue}}{\text{lb pesticide/A}}$

[2] Estimate of time from start of fruit formation to harvest.

RUD[1], ppm

0.5
3.5
0.5
0.3
0.2
1.4
0.3
0.25

2
3.2
1
3.2
4

2
0.8
1.8
4

1
1.7
0.5
1.3
1
1.3
0.7
0.4
0.25
1
1.3

0.4
1
1.3
0.25
1.3

3.3
0.38
2

for a number of pesticides on a number of crops were tabulated as illustrated in Table 7 for small fruits. For comparisons, the tolerance values have been converted to RUD. Tolerance values in the United States are established for a pesticide chemical, either on the basis that a commodity can be harvested immediately after treatment, or with the stipulation that the pesticide chemical not be used for a certain period before harvest. By considering the RUD values derived from tolerances of a number of pesticides on crops within a crop category, an empirical profile is obtained which represents residue levels at varying periods between treatment and harvest. Figure 1 is the profile or scatter diagram obtained by plotting the data in Table 7. It is seen that the highest RUD is 7 ppm on small fruit if a pesticide is applied 0 to 7 days before harvest, and it is about 1.5 ppm if applied 5 to 6 weeks before harvest.

Based on tabulations similar to Table 7, scatter diagrams show in Fig. 2 to 5 have been prepared for grasses and forage crops, pods containing seeds, grain and seeds, and large fruit, respectively. These categories were selected because of the large numbers

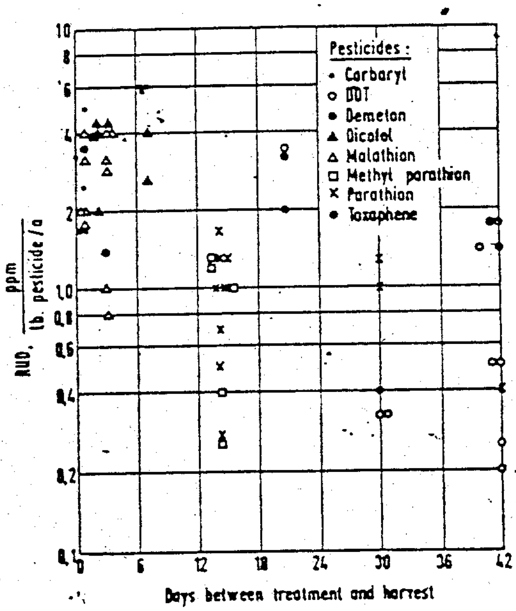

Fig. 1. Small Fruit. The Relationship Between RUD and the Interval Between Treatment and Harvest.
Data taken from 23 pesticide tolerances established by the Food and Drug Administration for residues in or on: blackberries and boysenberries (6 tolerances), blueberries (3), cherries (5), cranberries (4), currants (2), dewberries (4), gooseberries (2), grapes (7), loganberries (4), plums (7), raspberries (4), and strawberries (7).

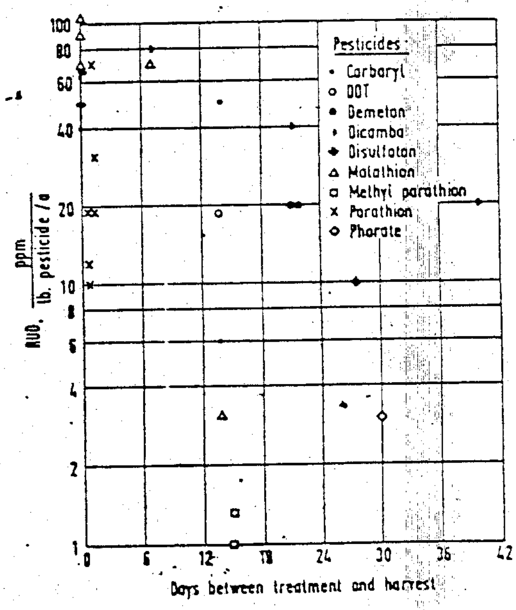

Fig. 2. Grasses and Forage Crops. The Relationship Between RUD and the Interval Between Treatment and Harvest.
Data taken from 29 pesticide tolerances established by the Food and Drug Administration for residues in or on: alfalfa (5 tolerances), barley (1), clover (5), corn forage (2), cotton forage (1), dandelion (2), grass pasture or range grass (5), pea forage (2), cow peas (1), peppermint and spearmint hay (1)' (plotted as greenforage), sorghum forage (2), and sugar beet tops (2).

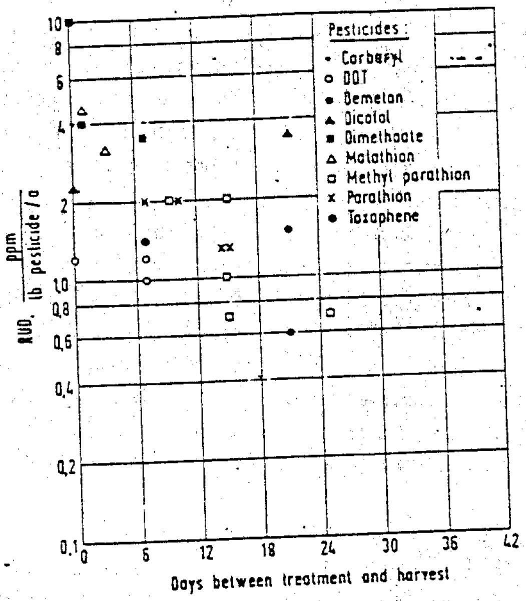

Fig. 3. Pods Containing Seeds and Shelled Pod Vegetables. The Relationship Between RUD and the Interval Between Treatment and Harvest.
Data taken from 23 pesticide tolerances established by the Food and Drug Administration for residues in or on: shelled cowpeas (1 tolerance), beans (3), green beans (4), lima beans (3), dry beans (3), black-eyed peas (1), shelled peas (7), and peas with pods (1).

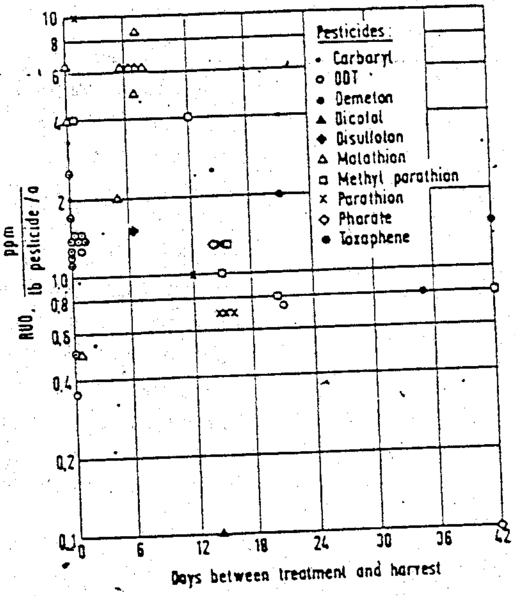

Fig. 4. Grain and Seeds. The Relationship Between RUD and the Interval Between Treatment and Harvest.
Data taken from 49 pesticide tolerances established by the Food and Drug Administration for residues in or on: barley (5 tolerances), dry beans (2), dry shelled lima beans (1), corn (5), cottonseed (6), oats (5), rice (6), rye (2), sorghum (5), soybeans (4), vetch seed (3), wheat (5).

of tolerances for crops in these categories and because of their greater relevance to the dietary intake of pesticide residues in the food of birds and other wildlife.

It should be noted that the data in Figures 1 to 5 represent 230 pesticides-crop combinations, 12 different pesticides, and 58 different crops. Almost all of the data in the scatter diagrams are for different crop-pesticide combinations than the data in Tables 1 to 5. The highest RUD values from each of the scatter diagrams are shown in Table 8. These values decrease in the sequence:

grass ⟩ pods containing seeds ⟩ grain ⟩ small fruit ⟩ large fruit

This sequence is similar to that shown in Table 6. The agreement in RUD values for pods containing seeds and for fruit in the two correlations shown in Tables 6 and 8 must be considered excellent.

Small fruit and large fruit were classified separately in order to establish whether there was a *difference in residue level* that correlated with a difference in surface/mass ratio. Small fruit show slightly higher residue values, but not nearly as great in magnitude as would be expected by the difference of surface/mass ratio. It is likely that differences in foliar interception ~~and protection~~ of the fruit, as well as differences in *retention characteristics* of the fruit surface, at least partially account for this limited correlation. Not much difference large - Small fruit

The highest RUD values derived from tolerance data for commodities harvested 5 to 6 weeks after pesticide application are also

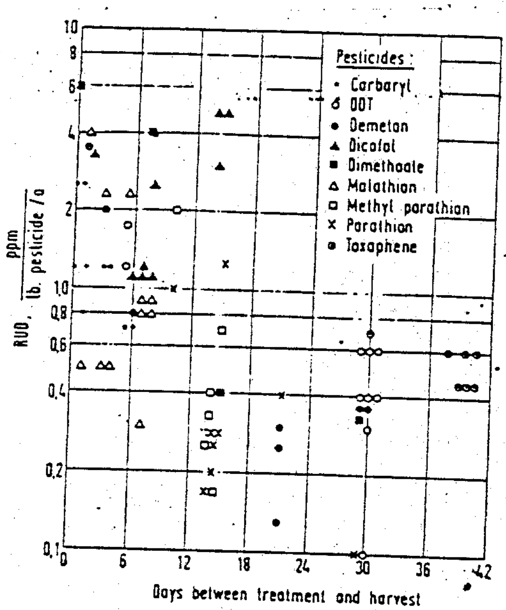

Fig. 5. Large Fruit. The Relationship Between RUD and the Interval Between Treatment and Harvest.
Data taken from 74 pesticide tolerances established by the Food and Drug Administration for residues in or on: apples (9 tolerances), apricots (8), avocado (3), citrus (8), crabapples (1), egg plant (7), figs (1), nectarines (7), olives (1), peaches (7), pears (9), pepper (1), quince (4), tomatoes (8).

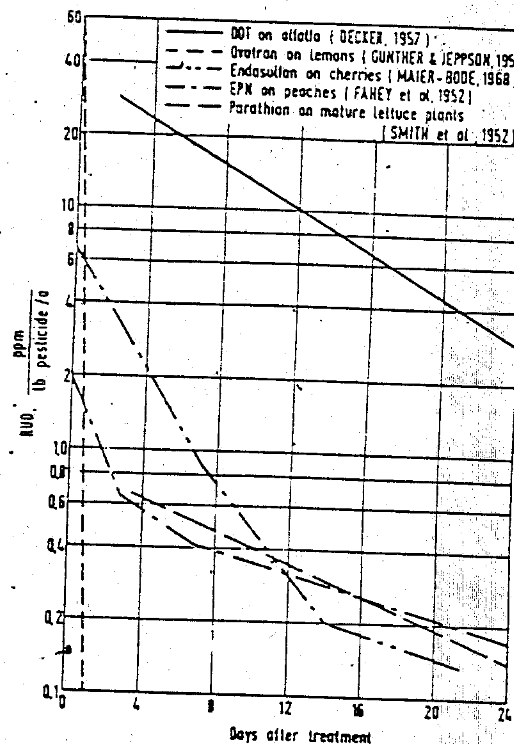

Fig. 6. Representative plots of the decline in pesticide residues illustrating the range of decline rates encountered with varying pesticide-plant combinations.

Table 8. Correlation of Representative Residue Tolerance Data: Highest Values of RUD According to Crop Category

Crop Category	*Highest RUD, Within 7 Days of Pesticide Treatment*	*ppm / lb Pesticide/A During 6th Week After Pesticide Treatment*
Grass	110	20
Pods Containing Seeds	10	1.5 (estimated)
Grain	10	1.5
Small Fruit	6	1.5
Large Fruit	6	0.6

shown in Table 8. It should be noted, however, that these values are based on only limited available tolerance data and that the data represent the more atypical slow decline of residue levels for the relatively small number of so-called "persistent" pesticides. In contrast, residue levels of a larger number of pesticides decline to low levels in a matter of a few days to a few weeks. For example, data in Figures 4 and 5 illustrate that residues of *malathion*, and *carbaryl* are frequently below 1 ppm within one week of harvest. Figure 6 illustrates the range of decline rates and the type of decline profiles that may be expected with different pesticide-plant combinations. Substantially complete disappearance of *parathion* from lettuce occurred within 1 day in contrast to a relatively slow disappearance of DDT from alfalfa.

Generalized Predictive Correlations

Summarizing, more than 250 different pesticide-crop combinations are represented by the data in Tables 1 to 5 and Figures 1 to 5. Considering that pesticide residues on plants decrease with time and that the cited data include several of the relatively small number of longer lasting, or so-called persistent pesticides, it seems reasonable that data from the tables and figures provide reasonable guidelines for *estimation of pesticide residues* in instances where experimental or field data are unavailable.

Therefore, Table 9 has been prepared as a reference for estimation of residues. It is derived from the summary data in Tables 6 and 8 and a few estimated values as described later. *Upper Limit* and *Typical Limit* values, two new terms used in Table 9, correspond to the highest residue and mean residue values, respectively, from Tables 6 and 8. *Upper Limit* and *Typical Limit* values are given for residue levels immediately after application of pesticide and for residue levels 6 weeks after application.

For each crop category, the *Upper Limit* value represents the highest level of residue resulting from application of pesticide, calculated on the basis of a dosage of 1 lb/A. It is believed that there is a very low probability of exceeding these *Upper Limit* residue values with pesticidal-cultural practices which are based on current technology, since the limits are extracted from extensive representative data and since the limits are consistent with considerations of surface/mass ratio, vegetative yield, and *interception factors.* These *Upper Limit* values therefore provide a very conservative basis for defining pesticide content of representative plant components.

It should be emphasized that more than 95 % of the actual residue values considered in this paper fall below the cited Upper Limit Values. Further, all of the data used in deriving the *Upper Limits* are weighted

Table 9. *Upper Limits and Typical Limits* of Residues of Pesticides on Differing Categories of Plants: Guidelines for Estimation of Residues [1]

Plant Category	*ppm Residue on the Basis of a Pesticide Dosage of 1 lb Per Acre (RUD)* — *Immediately After Application* — *Upper Limit*	*Typical Limit*	*6 Weeks After Application* — *Upper Limit*	*Typical Limit*
Range Grass	240	125	30	5
Grass	110	92	20	1–5
Leaves and Leafy Crops	125	35	20	<1
Forage Crops	58	33	1.0	<1
Pods Containing Seeds	12	3	1.5	<0.1
Grain	10	3	1.5	<0.1
Fruit	7	1.5	1.5	<0.2

[1] Summary and integration of data from Tables 6 and 8

toward extreme residue levels. The process of assigning tolerance values reflects the highest residue level observed under a number of different practical field conditions. Also, wherever the literature included multiple results, the highest reported value has been cited. For these reasons, more typical residue values are needed to properly represent the majority of *pesticidal-cultural practices.*

Therefore, *Typical Limit* values, shown in Table 9 and representing many types of pesticides, have been assigned on the basis of the arithmetical mean values cited in Table 6. In instances where the arithmetical mean data were not available, the *Typical Limit* values have been estimated empirically on the basis of disappearance implied by the scatter diagrams, the tabulated data, and Fig. 6. The *Typical Limit* residue values represent the limit of residue likely to result from application of pesticide, calculated on the basis of a dosage of 1 lb/A.

They are intended as *representative limiting values* for residues of any pesticide on plants within the crop category, except for the grouping of persistent and/or systemic pesticides.

The authors conclude that the *Typical Limit* values provide a realistic, yet moderately conservative basis for defining the pesticide content of food and feed items.

The main purposes of the predictive correlations shown in Table 9 are to:

1) Define quantitatively the *Upper Limits* of residue of any pesticide immediately after application.
2) Define quantitatively the *Upper Limits* of residues of even the most persistent pesticides that are to be expected over a period of time.
3) Permit *estimating the residue level of a pesticide on a given plant* from a basis which depends only upon developing an analogy between the surface/mass ratio, the vegetative yield, and the interception characteristics of the given plant and a spectrum of representative crop classifications.
4) Give an empirical set of *Typical Limit* values which may be used to realistically predict the fate of a pesticide when only exploratory laboratory data are available and thereby to permit more adequate decisions (a) on whether to commercialize a pesticide, and (b) on the selection of use patterns resulting in a minimum of environmental risk.
5) Provide residue data for toxicological safety calculations involving the dietary intake of pesticides by birds, other wildlife, and domestic animals.
6) Provide a basis for selecting relevant pesticide levels to be used (a) in conducting laboratory toxicological studies, or (b) in developing analytical methods with appropriate sensitivity.
7) Give a basis for comparison of the residues expected from pesticides of differing chemical, and physical properties.

Significance of Typical Limit Residue Values

For many purposes the *Typical Limit* values shown in Table 9 will be more useful than the *Upper Limit* values. Examples of conditions under which the *Upper Limit* values might be adjusted downward, even below, the *Typical values* are shown below. Theoretical bases for adjustment of the Limit values will be treated later.

1) *Exploratory laboratory and/or greenhouse data* indicate that a pesticide is relatively volatile (as might be indicated by vapor pressure data or by preliminary experiments indicating a decrease in pesticidal activity) over a limited period of time.
2) The pesticide is known to be relatively unstable to hydrolysis, oxidation, or photodegradation.
3) The plant or plant substrate of interest is grown under a protective canopy of brush, forest, or tall foliar plants (as the case for forest insect control) or under protective covering of the plants (as a seed covered by husk).
4) The plant or plant substrate has been treated with pesticide before its stage of rapid growth, e. g., grains before heading.
5) The plant or plant substrate has been exposed to a period of relatively high rainfall or wind.
6) The *conditions of application* are such that much of the pesticide is applied to the ground rather than retained by the foliar surface (granular or dust fomulations, or direct application to the soil).

Residues of a pesticide must ultimately be judged in respect to their toxicological significance. *Upper Limit* residue values reflect the most extreme and infrequent residue problems. *Typical Limit* residue values reflect the extreme of environmental conditions likely to occur. The *Typical Limit* residue values, along with judgmental modifications of their value, provide for greatly *increased reliability* in defining the toxicological significance of pesticides in the environment.

Therefore, the *Upper Limit* and *Typical Limit* values, when used judiciously, provide a basis for estimating the toxicological significance of pesticide residues in the food supply of man.

Theoretical Support for the Predictive Correlations

In the previous section it was illustrated that with some knowledge of a particular pesticidal-cultural practice, the Limit values might be adjusted to more realistically represent the environmental situation. It therefore is appropriate to review briefly the theory of some of the additional *parameters affecting residue levels.* Consideration of this theory permits greater reliability in use and extension of the *Limit values*. Additionally, this theoretical consideration affords a supportive understanding of the validity of the Limit values.

Dilution of Residues by Plant Growth. It is apparent that growth of a plant and resultant increase of plant mass results in a decrease in the weight fraction of residue in a plant substance. In some instances this dilution by plant growth is quite significant and occurs within a matter of only a few weeks. For example Sloan et al. (1951) showed that during the two-week period before harvest, growth alone accounted for a 73 % decrease in residue level of DDT on Iceberg lettuce. Similarly, Decker's (1957) data on residues of DDT on clover translate to an 84 % reduction in residue level for a 4 to 6 week growth period.

Dilution by growth, or perhaps more explicitly, the dependency of residue level upon the amount of vegetative cover, provides an explanation for the difference between the RUD of 240 ppm for picloram on range grass in Montana (Table 1) and the lower values for malathion (RUD of 110 ppm) and other pesticides on grass as derived from tolerance data (Fig. 2). Range grass provides a relatively low yield of forage per acre and the Montana experiment was conducted when the grass was at the boot stage of heading. Thus, the reported high residue of picloram is not unexpected. Data in Table 1 indicate that range grass from seven locations contained an average of 130 ppm picloram, a value more consistent with that reported by Morton for 2,4-D in range grass from Texas. RUD values of malathion and other pesticides shown in Fig. 2 are specified as grass in the tolerance listings. It is believed that pasture grass, more lush and higher yielding than range grass, was studied in experiments providing data for establishing tolerances.

A growth factor, explicitly the stage of growth, influenced the assignment of *Typical Limit* values (6 weeks after application) for pods containing seeds, grain, and fruit shown in Table 9. Plants producing seeds and fruit mature rapidly. Either the entire seed is formed or significant growth of fruit occurs during the six weeks period prior to maturity. A *Typical Limit* value of 0,2 ppm was assigned to fruit to account for slower growing citrus in contrast to a negligible value of 0.1 ppm for grain and seeds. It should be recalled that the *Typical Limit* values do not apply to the relatively small group of systemic herbicides. These will be discussed later.

Loss of Residues by Weathering. Whereas dilution by growth does not result in actual loss of pesticide, several factors, generally described by the term weathering, result in gradual loss of pesticide from plants. Rainfall

These factors include rain and humidity, sunshine (photodegradation), wind (mechanical abrasion and removal), temperature, and undoubtedly others. Ebeling (1963) cites illustrative data for the influence of these variables on residues. Since the effects of weathering factors are almost always interrelated, relatively few studies have isolated the quantitative effect of individual weathering factors under field conditions.

However, it should be emphasized that these weathering factors, in total, are significant. For example, residues of tricyclohexyltin hydroxide on grass were 60 ppm immediately after treatment, but decreased to one-half this value within 4 days (Getzendaner and Gentry, 1970). In contrast, residues of tricyclohexyltin hydroxide on apples decreased from 2 ppm immediately after spray treatment to one-half the initial value in 4 weeks (Getzendaner and Corbin, 1969). Based on a study of the data in Tables 1 to 5 of other pesticides, and the results of Gunther and Jeppson (1954) and Gunther et al. (1958A, 1958B), it seems reasonable to conclude that weathering effects will be greater when the ratio of surface/mass is high (grass), and that weathering effects will be minimized when the surface consists of a waxy or oily cuticular surface which is compatible with and "protects" low levels of the pesticides from weathering, e. g., apples or citrus fruit.

Chemical and Physical Properties of the Pesticide Affecting Loss of Residue. Kenaga (1968) cites a number of chemical and physical properties of pesticides which influence the degree of loss of pesticides from plant surfaces. 1 Volatility, 2 water solubility, and 3 chemical stability appear to be the more important of the pesticide properties that influence the degree of loss, mainly by influencing the rate of weathering. For example, DDT is quite chemically stable, is only very slightly soluble in water, and is of low volatility resulting in relatively high persistence on various surfaces. In contrast, parathion is relatively volatile, a factor which contributes to its relatively rapid disappearance from many plants surfaces. This rapid disappearance is illustrated by data in Tables 2 and 5, showing decreases of RUD values of 70 % to 91 % in 7 days on cabbage, celery leaves, and turnip greens and of 50 % on immature peaches in 7 days. Also, substantially complete loss of parathion from lettuce in one day is illustrated in Fig. 6.

It should be noted here that the apparent volatility of some pesticides from plant surfaces is increased under conditions of high humidity and/or the presence of moisture. Ebeling (1963) cites numerous literature examples. Harris and Lichtenstein (1961) have suggested that pesticide molecules are apparently displaced by water molecules from the air, resulting in an increase in the rate of volatilization. The tendency of a pesticide to remain *preferentially* adsorbed on plant surfaces in monomolecular or thin layers thus appears to be an important parameter in addition to inherent vapor pressure. Ultimately, most pesticides are degraded to simple compounds either on the plant surface, or after transfer to the soil or atmosphere. Pyrethrins and rotenone decompose rapidly when exposed to sunlight and air. TEPP and dichlorvos are alkylphosphates which hydrolyze very rapidly so that no toxic residues remain on plants after a matter of hours (Ebeling, 1963). Organic pesticides that are transferred from target vegetation to soil are usually ultimately degraded to simple and non-toxic compounds by soil microorganisms. Loss of the pesticide by volatility is usually followed by photodegradation, since dust particles or minute moisture particles provide ideal sites for adsorption of pesticide, and resultant exposure of thin films of pesticide (high surface/mass ratio), to ultraviolet energy and oxygen.

Another characteristic property of a pesticide is its relative tendency to be adsorbed and translocated by plants and/or insects. The systemic or non-systemic nature of a pesticide is influenced not only by its water solubility and water-lipid solubility partition coefficients, but also by the nature of the particular plant cuticular and transport systems. Although herbicidal or insecticidal activity of a pesticide is often dependent entirely upon foliar or root adsorption and upon translocation, the amount of systemic pesticide retained in plant tissue appears to be small in relation to the pesticide treatment rate or the sometimes high initial levels of foliar residues (Hoerger, 1970).

Concluding Comments

Briefly, consideration of three physical factors, vegetative yield, surface/mass ratio, and interception factors, permit classification of plants into categories which show a similarity in residue levels after application of pesticide. Consideration of an extensive data base permits assignment of numerical *Upper Limit* and *Typical Limit* residue values for each category of plants. Further reliability in estimating residues on plants can be achieved by theoretical consideration of the other parameters affecting pesticide residue levels. *Typical Limit* values provide a *realistic*, yet moderately conservative basis, for defining the pesticide content of food and feed items. The *Limit* values in Table 9 provide adequate accuracy for assessing the toxicological significance of the extremes of pesticide residue concentrations on plants as related to the food supply of man, domestic animals, birds, and other wildlife.

Zusammenfassung

Daten oder zuverlässige Schätzungen über die Höhe von Pestizidrückständen auf verschiedenen Pflanzenarten sind häufig erforderlich, um die toxikologische Bedeutung eines Pestizids in der Umwelt bewerten zu können. Dieser Bericht enthält und vergleicht Daten über Rückstände von über 20 Pestiziden auf über 60 Kulturpflanzenarten, die aus der Literatur und aus Erntegut-Toleranzen der Vereinigten Staaten entnommen sind. Unter Beachtung der Unterschiede im Wachstumsertrag, im Verhältnis von Pflanzenoberfläche zur Masse und in den pflanzlichen Hemmfaktoren wurden die Kulturpflanzen in 7 verschiedene Kategorien eingeteilt.

Auf der Grundlage von experimentellen Daten und von Toleranzdaten wurden für jede dieser Kategorien Zahlen für *Oberste Grenz-Rückstandswerte* und für *Typische Grenz-Rückstandswerte* angegeben, beide unmittelbar nach der Pestizid-Applikation und nach einer Wartezeit von 6 Wochen. Der *Oberste Grenz-Rückstandswert* und der *Typische Grenz-Rückstandswert* nehmen bei diesen Kategorien in der folgenden Reihenfolge ab:

Weidegras > Gras > Blätter und Blattpflanzen > Futterpflanzen > Hülsen mit Samen > Körner > Früchte.

Nach einer Pestizidanwendung von 1 lb/acre, liegen die *Obersten Grenz-Rückstandswerte* zwischen 240 ppm auf Weidegras und 7 ppm auf Früchten (unmittelbar nach der Applikation). Die *Typischen Grenz-Rückstandswerte* liegen zwischen 125 ppm und 1,5 ppm.

Die allmähliche Abnahme von Pestizidrückständen wurde erörtert im Zusammenhang mit dem Schätzen von Rückstandswerten in verschiedenen Zeitabständen nach der Pestizidanwendung. Die Grenzwertzahlen und das Betrachten der Faktoren, die die Abnahme beeinflussen, schaffen eine Grundlage für eine angemessene Abschätzung der Rückstände für andere Pflanzen, für die keine Daten zur Verfügung stehen — Schätzungen, die auf obigem Konzept beruhen, sorgen für größere Zuverlässigkeit bei der Definition der toxikologischen Bedeutung von Pestiziden im Hinblick auf die Nahrungsmittelversorgung von Menschen, Haustieren, Vögeln und anderen wildlebenden Tieren. In ähnlicher Weise kann die Bedeutung einer vorgeschlagenen landwirtschaftlichen Pestizidpraxis vor der allgemeinen Anwendung zuverlässiger bewertet werden.

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